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In-situ Mössbauer Spectroscopy with MIMOS II at Rio Tinto, Spain

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Abstract. The Rio Tinto, located in southwest Spain, exhibits a nearly constant, acidic pH-value along its course. Due to the formation of sulfate minerals, Rio Tinto is considered a potential analogue site for sulfate-rich regions on Mars, in particular at the landing site of the Mars Exploration Rover Opportunity, where the ferric sulfate mineral jarosite was identified with Opportunity's Mössbauer spectrometer. Primary and secondary mineralogy was investigated in situ with portable Raman and Mössbauer spectrometers at four different Rio Tinto sampling sites. The two techniques analyse different sample portions due to their specific field of view and sampling depth and provide complementary mineralogical information.

1. Introduction

The Rio Tinto, located in southwest Spain, exhibits a sulfate-rich mineralogy, linked to significant acidophilic biogenic activity. An important characteristic of the river is its nearly constant acidic pH value of ~2.3 along its approximately 100 km long course. Sulfates mainly form through aqueous alteration of iron-rich sulfide minerals of the Iberian Pyrite Belt [1]. The MER rovers identified sulfate minerals on the Martian surface. In Meridiani Planum, along the 14 km traverse of the rover Opportunity, jarosite was detected by the Miniaturised Mössbauer spectrometer MIMOS II [2-4]. The identification of sulfates and in particular jarosite provides clear mineralogical evidence for past water activity at Meridiani Planum and acidic conditions. The Rio Tinto region is thus considered a potential analogue site for Meridiani Planum. Micro-Raman and Mössbauer spectroscopy are among the techniques available for in-situ analyses on the Martian surface. Both instruments can be mounted on the robotic arm of a rover, constituting the contact-analytical forefront for surface mineral analysis. On a Mars mission, the combination of these techniques will provide definitive mineralogical and chemical identification of a great number of surface minerals and in particular of sulfates on Mars. To develop the operation methodology associated with mission objectives, in situ analyses were performed during a field campaign at Rio Tinto in June 2008.

For the in situ Mössbauer setup, two MIMOS II sensorheads were equipped with ⁵⁷Co-sources (~30 mCi). Spectra of good quality were obtained within less than two hours and at ambient temperatures of ~35 °C. The spot diameter for a measurement is 15 mm. MIMOS II sensorheads were also used for laboratory measurements. The enhanced follow-up version of the spectrometer, MIMOS IIA, will be equipped with silicon-drift-detectors (SDD) instead of Si-PIN detectors, thus providing a significantly

better signal-to-noise ratio. The instrument will also be able to measure X-ray fluorescence to determine elemental composition.

Raman spectra were obtained in-situ with a portable i-Raman from B&W TEC Inc, adapted to work under field conditions. The optical head was positioned in front of the samples using a mechanical device which allows mapping the surface at near the mineral grain scale. A baffle was used to minimise the solar light background. The excitation used was a 532nm wavelength laser with ~15 mW power on the sample and a spot diameter of 100µm. Spectral resolution was 5 cm⁻¹.

To characterize the samples with an independent laboratory method, XRD measurements were recorded on finely ground samples using a Bruker AXS D8 Advance diffractometer with MoK α radiation and a SolX energy-dispersive detector in Bragg-Brentano mode.

2. Results

Four different sampling sites were studied with the aim of investigating primary volcanic rocks and different stages of weathering due to hydrological activity and evaporite minerals as the direct product of the acidic water evaporation mediated by acidophilic activity. Measurements were performed in-situ on evaporative precipitates and bedrock. Due to time constraints, Raman and Mössbauer spectra were not always taken on the exact same spot, but in close proximity to each other. In addition to the in-situ measurements, representative samples from all sampling sites were analysed in detail after the field trip with the laboratory instrument setups.

Outcrops of primary volcanic rock were investigated a few kilometers from the river. These show some signs of weathering on the surface and, due to water circulation, along minor cracks. Spectra were obtained on a drill core, which included surface material and a crack. Mössbauer spectra show a ferrous doublet, a ferric doublet and a sextet (Figure 1a). The ferrous doublet, with an isomer shift of 1.14 mm/s and a quadrupole splitting of 2.73 mm/s stems most likely from chlorite crystals in the sample. The ferric doublet, with an isomer shift of 0.36 mm/s and a quadrupole splitting of 0.69 mm/s, can be attributed to superparamagnetic goethite. The sextet, with an isomer shift of 0.39 mm/s and a magnetic hyperfine field of 51.9 T, can be attributed to hematite. Raman measurements confirmed the presence of goethite and hematite and revealed the silicate phases quartz and muscovite, which do not contain iron and are therefore not detectable in Mössbauer spectra.

Porous volcanosedimentary materials originally constituted the rock complex at the Pena de Hierro site (e.g., Figure 1 from [1]) before they were affected by hydrothermal fluids, forming rocks rich in quartz, other silicates and pyrite. Acidic weathering driven by microbial activity then led to the replacement of the sulfide ore body by gossan [5]. The resulting rocks contain black, hard material intermixed with red, softer material. A representative spectrum is shown in Figure 1b, with contributions from a ferric doublet and magnetic components. The ferric doublet with an average isomer shift of 0.37mm/s and an average quadrupole splitting of 0.64 mm/s can be attributed to superparamagnetic goethite. XRD analyses confirmed the presence of goethite in these samples instead of other iron oxides which would be consistent with the Mössbauer parameters. Crystalline goethite is also present in most of the samples, characterized by Mössbauer sextets with a distribution of magnetic hyperfine fields ranging from 26T to 38T. Most spectra show hematite with an average isomer shift of 0.37mm/s and an average magnetic hyperfine field of 51T. Some samples contain hematite with different degrees of crystallinity. Well-crystalline hematite shows a larger magnetic hyperfine field and smaller line widths. Silicate phases were detected in some samples based on a ferrous doublet in their Mössbauer spectra. The presence of hematite with different degrees of crystallinity and goethite were confirmed by Raman analyses. In addition to iron-bearing minerals, epsomite (Mg(SO₄)·7(H₂O)) and quartz were detected through Raman and XRD measurements, respectively.

The lithified sedimentary deposits at the “Huerto del Loco” area (e.g., Figure 1 from [1]) were found to be conglomeratic, cemented materials with clast sizes in the range up to ~3cm. The surface of the rocks is in many cases visibly affected by the acidic water and exhibits a dark crust. Several samples from the river bedrock and a drill core were taken for laboratory analyses. Mössbauer spectra

show a prominent ferric doublet with an average isomer shift of 0.37 mm/s and an average quadrupole splitting of 0.54 mm/s, attributed to superparamagnetic goethite. Again, XRD analyses confirmed the presence of goethite instead of other iron oxides. Minor amounts of hematite are also present. Some clasts show ferrous doublets due to silicate phases. Raman spectra confirm the presence of goethite and hematite and identify quartz as the main silicate phase in the matrix. Two spectra obtained from the drill core are shown in Figure 1c and d.

Efflorescent precipitates and evaporite crusts can be observed as seasonal deposits in a number of locations close to the stream margin. During our field campaign, precipitates with “popcorn”-like texture a few cm in diameter were most common, their main colors were white and different shades of yellow, sometimes mixed with small amounts of red or grey. Loose crusts up to ~5mm thick and up to a few cm in diameter were encountered on some rocks close to the water, exhibiting a variety of colors including white and different shades of green and blue. A representative amount of crusts was sampled for laboratory analyses. As evaporite minerals may easily be altered by a change of their environment (e.g., temperature and humidity), representative samples were analysed in situ. Typical integration times in the field were between 30 minutes and two hours. The samples studied in situ were again analysed with laboratory equipment after ~ 8 weeks, mineralogical changes could not be detected.

The Mössbauer spectra of “Popcorn-texture” evaporites exhibit single ferric doublet, with an average isomer shift of 0.42 mm/s and an average quadrupole splitting of 0.55 mm/s (Figure 1e). This doublet results from a mixture of the ferric sulfates copiapite ($\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)(\text{OH})_2 \cdot 20\text{H}_2\text{O}$) and coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$), which can be detected separately in Raman spectra. In addition to copiapite and coquimbite, minor amounts of rhomboclase ($(\text{H}_5\text{O}_2)^+\text{Fe}^{3+}(\text{SO}_4)_2 \cdot 2(\text{H}_2\text{O})$), were detected in XRD measurements. Mössbauer spectra obtained on white, green and blue crusts show a single ferrous doublet with an average isomer shift of 1.25 mm/s and an average quadrupole splitting of 3.1 9mm/s (Figure 1f), resulting from the ferrous sulfates melanterite ($\text{Fe}^{2+}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$) and rozenite ($\text{Fe}^{2+}(\text{SO}_4) \cdot 4(\text{H}_2\text{O})$), which can be distinguished in Raman and XRD analyses.

Portions of the river bedrock were covered with a red crust, in which jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) was detected with the Mössbauer and the Raman spectrometer. A spectrum was obtained on red crust on top of black substrate. It shows pyrite from the substrate layer, with an isomer shift of 0.33mm/s and a quadrupole splitting of 0.59 mm/s, and jarosite from the red crust with an isomer shift of 0.37mm/s and a quadrupole splitting of 1.18 mm/s (Figure 1g). Sometimes, an additional, thin, white or yellow crust covers the red crust. A spectrum obtained on light crust on top of red crust is shown in Figure 1h. Jarosite from the red crust and copiapite with coquimbite from the light crust were clearly detected. In this spectrum, jarosite and copiapite have similar isomer shifts of ~0.38 mm/s, but different quadrupole splittings of 1.15 mm/s and 0.55 mm/s, respectively. MIMOS II is able to measure two layers simultaneously. Different subspectral areas of mineral phases from both layers result from their thickness and Fe content. Raman spectra obtained on this sample show copiapite or coquimbite from the light colored top layer, jarosite was detected at some spots.

A stream with a slightly higher pH-value (~3.5) runs parallel to the Rio Tinto close to its source. Orange sediment was sampled and dried for laboratory analyses. With an isomer shift of 0.36 mm/s and a quadrupole splitting of 0.61 mm/s, it was identified as schwertmannite ($\text{Fe}^{3+}_{16}\text{O}_{16}(\text{OH})_{12}(\text{SO}_4)_2$). The spectrum (shown in Figure 1i) shows a slight asymmetry, as has been reported for schwertmannite previously [6].

3. Conclusions

Mössbauer- and Raman- spectroscopy provide complementary information about a sample: Raman spectroscopy is sensitive to the very surface of a sample, and the Raman field of view is small enough (~100 μm) to perform measurements at the scale of single mineral grains. With its field of view of ~1.5 cm and sampling depth of ~200 μm , MIMOS II provides mineralogical context information about a larger volume and depth selective information about a sample by detecting backscattered 14.4 keV γ - and 6.4 keV X-rays simultaneously [7]. The two instruments also provide complementary mineralogical information: While Raman spectroscopy is sensitive to a large number of minerals and

organic phases, Mössbauer spectroscopy provides detailed information about Fe-bearing mineral phases, Fe oxidation states and the distribution of Fe among them. Redox cycling of Fe can provide energy for microbial metabolism [e.g. 8]. Raman and Mössbauer spectroscopy may prove to be a valuable combination to determine organic phases and Fe oxidation states to search for past or present traces of life on Mars.

Acknowledgements

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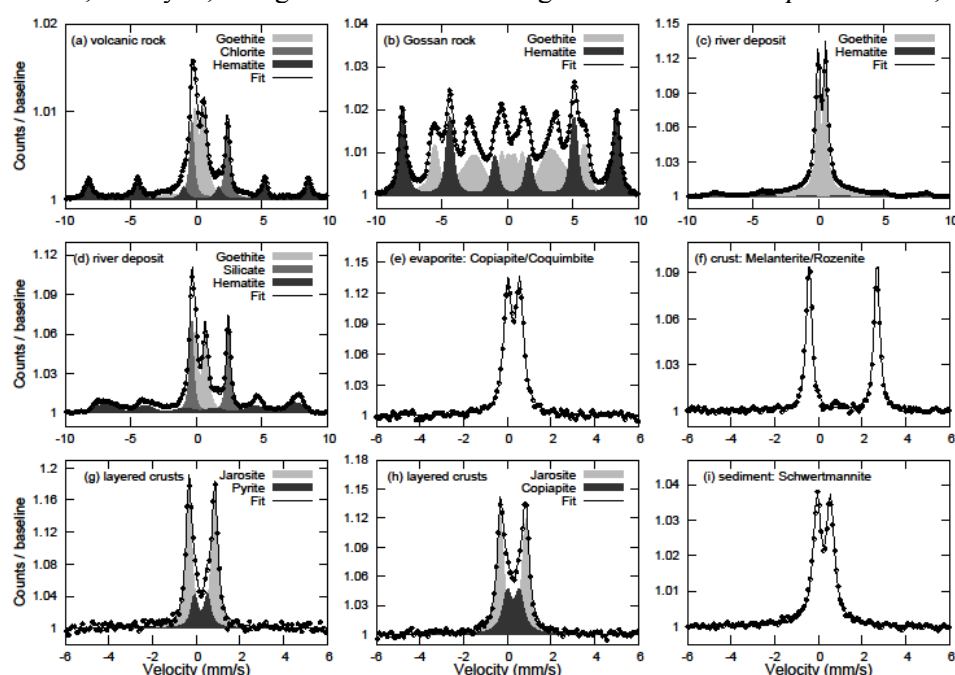


Figure 1: representative spectra from Rio Tinto samples: (a) Volcanic outcrops show minor amounts of weathering phases such as hematite and goethite. (b) Gossan rocks show mixtures of hematite and goethite. (c, d) conglomeratic river deposits are dominated by nanophase goethite and hematite. (d) Ferrous doublets due to silicate clasts are also observed. (e) The common popcorn texture evaporites are dominated by copiapite and coquimbite. (f) Ferrous sulfates (melanterite, rozenite) were identified in crust precipitates. (g) A layered sample of red crust on top of black substrate shows jarosite from the crust and pyrite from the substrate. (h) Light crust on top of red crust shows copiapite from the light crust and jarosite from the red crust. (i) Schwertmannite was identified in river sediment.